#### 1.1. Basic concepts

1.1-1. Give the units of physical quantities defined by the expressions below

$$-\int_{V_1}^{V_2} p_{prac} dV; \quad \left(\frac{\partial U}{\partial T}\right)_V dT; \quad \left(\frac{\partial p}{\partial T}\right)_V; \quad \left[-p + T\left(\frac{\partial p}{\partial T}\right)_V\right] dV; \quad \frac{dn_i}{v_i}$$

gas constant, Boltzmann constant, Faraday constant

#### 1.1-2. Calculate the indicated derivatives

a) 
$$PV = nRT$$
;  $P$  with respect of  $V$   
b)  $d = \frac{m}{V}$ ;  $\left(\frac{\partial d}{\partial m}\right)_{V} = \left(\frac{\partial d}{\partial V}\right) =$   
c)  $\rho = \frac{PM}{RT}$ ;  $\rho$  with respect of  $T$   
d)  $H = a + bT + cT^{2} + \frac{d}{T}$ ;  $H$  with respect of  $T$   
e)  $\left(P + \frac{n^{2}a}{V^{2}}\right)(V - nb) = nRT$ ;  $P$  with respect of  $V$   
f)  $V = \pi r^{2}h$ ;  $\left(\frac{\partial V}{\partial r}\right)_{h} = \left(\frac{\partial V}{\partial h}\right)_{r} =$ 

**1.1-3.** Sketch the curves of the coefficient of isothermal expansion and compressibility for an ideal gas.

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T,\xi}$$

#### 1.1-4. Write an expression for the total differential of the following quantities:

 $V = f(r,h) = \pi r^2 h \qquad c^2 \frac{2kT}{m} \qquad V = 1001.93 + 111.5282m + 0.64698m^2$  $\ln p = \frac{-\Delta H}{Rt} + K \qquad \qquad w = N \ln N - n_i \ln n_i$ 

#### 1.1-5. Calculation of errors of a complex function using the total differential method.

a) Calculate the absolute error of the measurement of the molar concentration of sodium hydroxide, knowing that a technical scale was used to weigh the mass, the volume was measured with a burette, and the mass numbers were read from the periodic table, rounded from integers. Data: m=100g, V=500ml.

b) Calculate the absolute error of the measurement of the percentage concentration of potassium hydroxide, knowing that an analytical balance was used to weigh the KOH mass, and a technical balance was used to weigh the water.

Data: m<sub>KOH</sub>=10.0000g, m<sub>water</sub>=500.0g.

# 1.2. First law of thermodynamics

# 1.2.1. Gas laws, ideal gases

# 1.2.1-1.

A perfect gas undergoes isothermal compression, which reduces its volume by 1.80 dm<sup>3</sup>. The final pressure and volume of the gas are 1.97 bar and 2.14 dm<sup>3</sup>, respectively. Calculate the original pressure of the gas in (a) bar, (b) Torr.

# 1.2.1-2.

A sample of hydrogen gas was found to have a pressure of 125 kPa when the temperature was 23°C. What can its pressure be expected to be when the temperature is 11°C?

# 1.2.1-3.

A homeowner uses  $4.00 \times 10^3$  m<sup>3</sup> of natural gas in a year to heat a home. Assume that natural gas is all methane, CH<sub>4</sub>, and that methane is a perfect gas for the conditions of this problem, which are 1.00 atm and 20°C. What is the mass of gas used?

# 1.2.1-4.

What pressure difference must be generated across the length of a 15 cm vertical drinking straw in order to drink a water-like liquid of density  $1.0 \text{ g cm}^{-3}$ ?

# 1.2.1-5.

Calculate the mass of water vapour present in a room of volume 250  $\rm{m^3}$  that contains air at 23°C on a day when the relative humidity is 53 per cent.

# 1.2.1-6.

A manometer like that described in Exercise 1.6a contained mercury in place of water. Suppose the external pressure is 760 Torr, and the open side is 10.0 cm higher than the side connected to the apparatus. What is the pressure in the apparatus? (The density of mercury at 25°C is 13.55 g cm<sup>-3</sup>.)

# 1.2.1-7.

At 100°C and 16.0 kPa, the mass density of phosphorus vapour is  $0.6388 \text{ kg m}^{-3}$ . What is the molecular formula of phosphorus under these conditions?

# 1.2.1-8.

A gas mixture consists of 320 mg of methane, 175 mg of argon, and 225 mg of neon. The partial pressure of neon at 300 K is 8.87 kPa. Calculate (a) the volume and (b) the total pressure of the mixture.

# 1.2.1. Quantification of work, heat exchange, and heat capacity

# 1.2.1-1.

Calculate the volumetric work done by the reaction of three moles of sodium with water at 20°C.

# 1.2.1-2.

A mass of  $2 \cdot 10^{-3}$  kg of Helium at a temperature of 273 K and a pressure of  $2 \cdot 10^{-5}$  Pa is expanded isothermally to a volume of  $2 \cdot 10^{-3}$  m<sup>3</sup>. Calculate the work done by the system.

# 1.2.1-3.

A chemical reaction takes place in a tank whose cross-sectional area is 100cm<sup>3</sup>. The tank is closed at one end by a free-moving piston. As a result of the reaction, the piston moves 10cm, overcoming a pressure of 1.0 atm. Calculate the work done by the system.

# 1.2.1-7

In the isothermal reversible compression of 52.0 mmol of an ideal gas at 260 K, its volume is reduced to one third of its initial volume. Calculate the work W in this process.

# 1.2.1-4.

When 229 J of heat is added to 3.0 moles of Ar(g) at constant pressure, the temperature of the sample increases by 2.55 K. Calculate the molar heat capacity of this gas at constant pressure and constant volume.

# 1.2.1-5.

The mass of a typical sugar cube (sucrose) is 1.5 g. Calculate the amount of energy released when it burns in air. How high could a 65 kg person climb after eating such a sugar cube, assuming that 25% of the energy is used for work?

# 1.2.2. Heat balance

# 1.2.2.-1.

A closed bottle with a volume of  $V_0$  = 500 cm3 contains mineral water at a temperature of  $t_0$  = 20°C. After some time, the sun heated the bottle to a temperature of tk = 40°C. Calculate how much solar energy the bottle absorbed.

Given: mass of glass  $m_{glass} = 300$  g, specific heat of glass  $c_{glass} = 0.75$  kJ/(kg K), specific heat of water  $c_w = 4.18$  kJ/(kg K), density of water  $d_w = 1$  g/cm<sup>3</sup>.

# 1.2.2-2.

Do styropianowego kubka z herbatą o masie  $m_h = 100$  g i temperaturze  $t_h = 80^{\circ}$ C wrzucono kostkę lodu o masie  $m_L = 20$  g i temperaturze  $t_L = -5^{\circ}$ C. Cała kostka lodu uległa stopieniu. Oblicz temperaturę końcową herbaty przy założeniu, że wymianę ciepła układu z otoczeniem można zaniedbać. Dane: ciepło właściwe wody  $c_w = 4.18$  J/(g deg), ciepło właściwe lodu  $c_{wL} = 2.09$  J/(g deg), ciepło topnienia lodu  $q_{tL} = 332$  J/g.

# 1.2.2-3.

Estimate the cost of boiling water at a temperature of t0 = 15oC in an electric kettle with a power of P = 2000 W and a capacity of 1.5 litres. Assumption: process efficiency  $\eta$  = 80%, price of electricity per 1 kWh p = 0.1 euro.

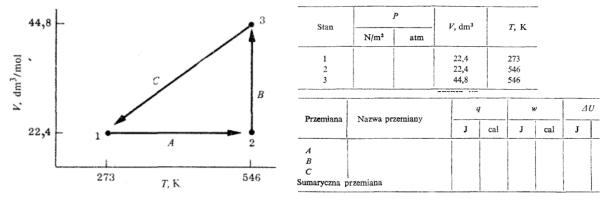
#### 1.2.3. Internal energy, 1st law of thermodynamics

#### 1.2.3-1.

Three moles of water are evaporated isothermally at 373 K and isobarically at 101.3 kPa. The molar heat of vaporization of water is 40.66 kJ·mol-1. Calculate the change in internal energy in this process.

# 1.2.3-2.

1 mole of a monatomic ideal gas undergoes a closed cycle of three reversible transformations A, B and C and successively reaches states 1, 2 and 3. Determine the missing values in the tables.



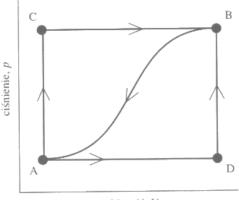
#### 1.2.3-3.

When the system moves from state A to B along path ACB (figure below), 80 J of heat flows into the system and 30 J of work is done by the system.

a) How much heat flows into the system along path ADB if the work done is 10 J?

b) When the system returns from state B to A along the indicated curve, the work done on the system is 20 J. Does the system absorb or release heat, and how much?

c) If Ud – Ua = + 40 J, calculate the heat absorbed in processes AD and DB.



objętość, V

#### 1.2.3-6.

A sample containing 1.00 mol H2O (g) undergoes isothermal reversible condensation at 100°C. The standard enthalpy of vaporization of water at 100°C is 40.656 kJ·mol<sup>-1</sup>. Calculate *w*, *q*,  $\Delta U$ ,  $\Delta H$  for this process.

#### 1.2.4. Enthalpy, Hess's Law; Thermochemical Calculations, Kirchhoff's Law

# 1.2.4-1.

Calculate the change in internal energy resulting from the following chemical reactions under standard conditions, according to the given stoichiometric equations:

a) 
$$Zn_{(s)} + H_2SO_{4(c)} = ZnSO_{4(s)} + H_{2(g)}$$
  $\Delta H_r^o = -152 \ kJ$   
b)  $N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)}$   $\Delta H_r^o = -92.0 \ kJ$ 

### 1.2.4-2.

Calculate the enthalpy change resulting from heating 5 moles of hydrogen sulphide from 373 K to 473 K at constant pressure, knowing that the molar specific heat of  $H_2S$  changes according to the equation:

$$C_p = 36.86 + 0.0079 T$$

# 1.2.4-3.

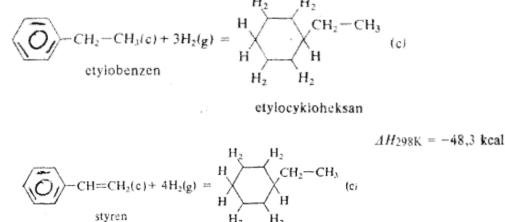
The heat of formation of C<sub>2</sub>H<sub>5</sub>OH<sub>(I)</sub> is -276 kJ/mol (-66 kcal/mol), while the heat of combustion of the isomer CH<sub>3</sub>OCH<sub>3(g)</sub> do CO<sub>2(g)</sub> i H<sub>2</sub>O<sub>(I)</sub> is -1456 kJ/mol (-348 kcal/mol). Furthermore, it is known that the heat of formation of H<sub>2</sub>O<sub>(I)</sub> is -285 kJ/mol (-68 kcal/mol), and the heat of combustion of carbon to CO<sub>2(g)</sub> is -393 kJ/mol (-94 kcal/mol). All data refer to a temperature of 25°C.

a) Calculate  $\Delta H_{298K}$  of the isomerization reaction: C<sub>2</sub>H<sub>5</sub>OH<sub>(I)</sub> = CH<sub>3</sub>OCH<sub>3(g)</sub>

b) Assuming that  $\Delta H_{298K}$  of this reaction is -41.8 kJ (-10 kcal), calculate  $\Delta U_{298K}$ 

# 1.2.4-4.

Using the following data:



$$\Delta H_{298K} = -74,65$$
 kcal

heat of combustion of ethylcyclohexane to  $CO_{2(g)}$  i  $H_2O_{(g)}$ : -5180.8 kJ/mol, the heat of formation  $H_2O_{(g)}$ : -244.0 kJ/mol, the heat of formation  $CO_2(g)$ : -393.5 kJ/mol (these data refer to a temperature of 298 K), calculate:

a) the heat of hydrogenation of styrene to ethylbenzene and

b) the heat of formation of ethylbenzene.

#### 1.2.4-5.

As a result of combustion of 0.5 g of naphthalene ( $M = 128.2 \text{ g} \cdot \text{mol}^{-1}$ ) in a bomb calorimeter, the temperature of the system increased by 1.92°C. The heat capacity of the calorimeter system is K = 10.47 kJ·K-1, and the average measurement temperature is about 25°C. Calculate the molar heat of combustion of naphthalene at constant pressure and the given temperature.

### 1.2.4-6.

The value of  $C_{p,m}$  for an ideal gas sample is found to vary with temperature according to the expression  $C_{p,m} = 20.17 + 0.3665$ . Calculate q, w,  $\Delta U$ , and  $\Delta H$  for 1.00 mole of this gas as the temperature increases from 25°C to 200°C a) at constant pressure, b) at constant volume.

# 1.2.4-7.

From the standard enthalpy of combustion, calculate the standard enthalpy of formation of butane at 25°C.

# 1.2.4-8.

After burning 120 mg of naphthalene,  $C_{10}H_8(s)$ , the temperature in the bomb calorimeter increased by 3.05 K. Calculate the calorimeter constant. By how much will the temperature increase if we burn 100 mg of phenol,  $C_6H_5OH_{(s)}$ , under the same conditions?

#### 1.2.4-9.

After burning 0.3212 g of glucose in a bomb calorimeter with a constant of 641  $J \cdot K^{-1}$ , the temperature increased by 7.793 K. Calculate: a) the standard molar energy of combustion, b) the standard internal energy of combustion, and c) the standard enthalpy of formation of glucose.

# Assessment

# A1.-1.

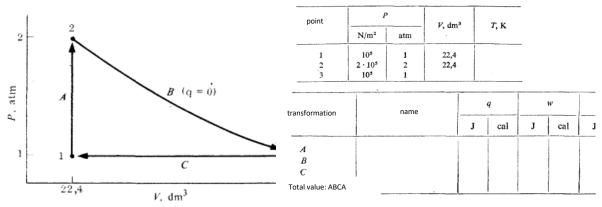
A 15 g magnesium ribbon is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of this reaction. The atmospheric pressure is 1.0 atm and the temperature is 25°C.

# A1.-2.

Steel hardening consists in rapid cooling of the heated metal. After throwing steel with a mass of  $m_s = 5$  kg and a temperature of  $t_s = 800^{\circ}$ C into water with a mass of  $m_w = 20$  kg and a temperature of  $t_w = 20^{\circ}$ C, 1% of the water evaporated. Calculate the final temperature of the water together with the hardened element, assuming that the heat exchange of the system with the environment can be neglected. Given: specific heat of water  $c_w = 4.18$  J/(g deg), heat of vaporization of water  $q_v = 2260$  J/g, specific heat of steel  $c_s = 0.46$  J/(g deg).

# A1.-3. 3

mole of a monatomic ideal gas undergoes three successive reversible changes, as illustrated in the figure below. Determine the missing values in the tables.



# A1.-4.

A system consisting of 9 g of solid H<sub>2</sub>O at 263 K is heated to form steam at 413 K. Calculate the enthalpy change  $\triangle$ H for this change. The specific heat of ice is 2.09 J·g<sup>-1</sup>·K<sup>-1</sup>. The heat of fusion of ice is 333.94 J·g<sup>-1</sup>, the heat of vaporization of water is 2261.34 J·g<sup>-1</sup>, the specific heat of water vapor 33.98 J·mol<sup>-1</sup>·K<sup>-1</sup>.

# A1.-5.

A sample containing 1.00 mol of Ar was subjected to isothermal expansion at 0°C from a volume of 22.4 L to 44.8 L assuming:

a) in a reversible manner,

b) under a constant external pressure equal to the final gas pressure,

c) in a free manner (at zero external pressure).

Calculate q, w,  $\Delta U$  and  $\Delta H$  for all three cases.